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# TECHNICAL NOTE

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## EXPERIMENTAL STUDIES ON BOWEN'S DECARBONATION SERIES, II.

P-T UNIVARIANT EQUILIBRIA OF THE REACTION:



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**EXPERIMENTAL STUDIES ON  
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P-T UNIVARIANT EQUILIBRIA OF THE REACTION:  
FORSTERITE + CALCITE = MONTICELLITE + PERICLASE + CO<sub>2</sub>**

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**SUMMARY**

The P-T univariant equilibrium curve for reaction A, calcite + forsterite = monticellite + periclase + CO<sub>2</sub>, has been experimentally determined to pass through the points: 725°C, 1300 psi<sub>CO<sub>2</sub></sub>; 850°C, 4400 psi<sub>CO<sub>2</sub></sub> and 925°C, 10,000 psi<sub>CO<sub>2</sub></sub>. The curve is coincident, within the limits of experimental error, with curves for reactions B and C: 2 calcite + forsterite + diopside = 3 monticellite + 2CO<sub>2</sub>, and calcite + diopside = akermanite + CO<sub>2</sub>, respectively. The P<sub>CO<sub>2</sub></sub>-T field of stability of the assemblage monticellite-forsterite-calcite-CO<sub>2</sub> which lies between the curves for reactions A and B is thus very small. The forsterite-calcite assemblage is usually produced by contact metamorphism by granitic rock types. Equilibrium pressure curves for reaction A are derived.



## CONTENTS

Summary . . . . .	i
INTRODUCTION . . . . .	1
EXPERIMENTAL PROCEDURE . . . . .	1
RESULTS . . . . .	2
DISCUSSION . . . . .	4
Critical Assemblages . . . . .	4
Equilibrium Pressure Curves . . . . .	5
Natural Occurrence of Pertinent Assemblages . . . . .	6
ACKNOWLEDGMENTS . . . . .	6
References . . . . .	7

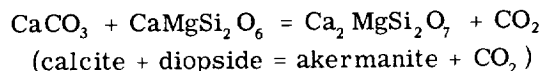
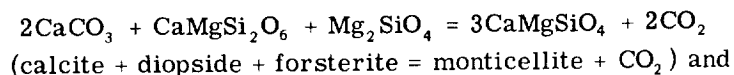


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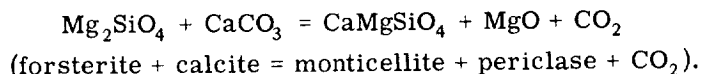
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**INTRODUCTION**

This is the second paper in a series presenting the results of experimental investigation of decarbonation reactions. Considering the effect of rising temperature at constant CO<sub>2</sub> pressure on the phases in the CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub> system, Bowen (Reference 1) proposed that, after the formation of monticellite and akermanite by the reactions:



the next logical step in decarbonation was represented by the reaction:



**EXPERIMENTAL PROCEDURE**

Many of the experimental techniques were described in the first paper of this series (Reference 2). Reagent-grade CaCO<sub>3</sub> and MgO were used as sources of calcite and periclase; monticellite and forsterite were prepared by heating appropriate oxide mixes to 1400 °C.

The samples were run in cold-seal pressure vessels using CO<sub>2</sub> as pressure medium and were contained in gold-foil envelopes which were pervious to the gas. In each run both the low and the high temperature assemblages, contained in separate envelopes, were used as starting mixtures.

Reaction rates were too slow to permit complete reaction at all times, except when runs were purposely placed at some distance from the univariant pressure-temperature (P-T) curve for this reaction. Therefore determination of the curve was dependent on recognition of the reaction's beginning. The addition of a small amount of distilled water (about 15-30 mg) to the pressure vessel before the runs increased the rate of reaction considerably. This water represented approximately 3 mole percent of the vapor in the pressure vessel, which has a capacity of 5cm<sup>3</sup>.

Determination of small amounts of monticellite produced by the reaction of forsterite and calcite was made on the basis of the presence of the strong x-ray diffraction line of monticellite at  $50.4^\circ 2\theta$  ( $\text{Cu K}\alpha$ ,  $d = 1.8105\text{\AA}$ ). The small amount of periclase produced by reaction could not be detected, probably because it reacted with the vapor to produce magnesite upon quenching. Even when run in the P-T stability region in which the monticellite-periclase assemblage was compatible with  $\text{CO}_2$ , this assemblage yielded a small amount of carbonate upon quenching. When this assemblage reacted, however, a large quantity of calcite was produced. With the use of a petrographic microscope, this was easily distinguishable from quench carbonate by its greater abundance. In most cases, forsterite could be identified as a product of a run by x-ray diffraction techniques.

## RESULTS

The univariant P-T curve determined for the "monticellite-periclase" reaction is shown in Figure 1, and the data for the critical runs are listed in Table 1.

The triangles shown in Figure 1 indicate the positions of some of the phases in the compositional tetrahedron  $\text{CaO-MgO-SiO}_2\text{-CO}_2$ . Carbon dioxide is envisioned at the apex of the tetrahedron, which is above the plane of the paper. Those phases which can coexist with the vapor are on, or projected onto, the base and are connected by solid lines. Calcite thus appears at the lower left-hand corner. Three crystalline phases which are mutually stable with  $\text{CO}_2$  are shown at the corners of compatibility triangles. This method of projection is more fully described by Bowen (Reference 1).

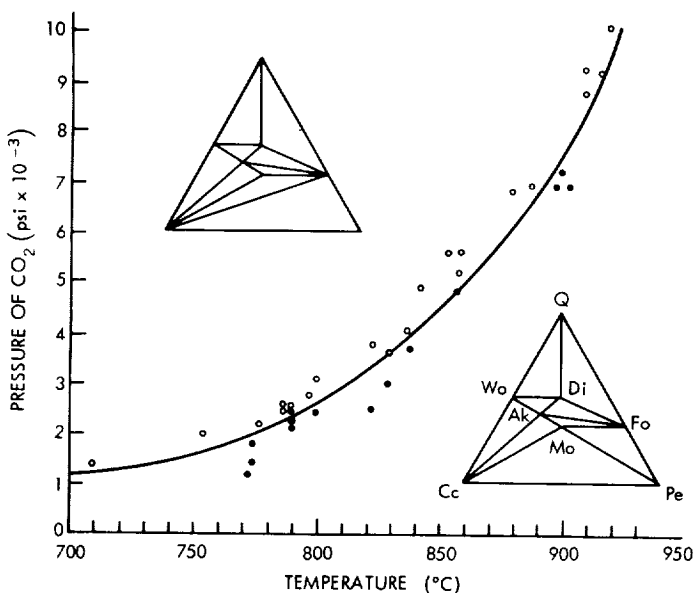


Figure 1—Experimentally determined univariant pressure-temperature curve for the reaction: forsterite + calcite = monticellite + periclase +  $\text{CO}_2$ .

The experimental error is considered to be  $\pm 7^\circ\text{C}$  and  $\pm 5$  percent of the total pressure. The P-T curve shown in Figure 1 is coincident, within the limits of experimental error, with the curves for the formation of monticellite and akermanite reported in the first paper. No explanation can be offered for this relationship.

Because they are located so close together, there is a possibility of the intersection of the P-T curves for the reactions  $\text{Fo} + \text{Cc} = \text{Mo} + \text{Pe} + \text{CO}_2$  and  $2\text{Cc} + \text{Fo} + \text{Di} = 3\text{Mo} + 2\text{CO}_2$ . The intersection would necessitate an invariant point which is illustrated, diagrammatically, in Figure 2. The spatial relationship

\*The following abbreviations will be employed: Cc = calcite, Fo = forsterite, Pe = periclase, Mo = monticellite, Di = diopside, Q = quartz, and Wo = wollastonite.



Table 1  
Data Used to Determine the Location of the Univariant  
Pressure-Temperature Curve for the Reaction:  
 $Cc + Fo = Mo + Pe + CO_2$ .

Temperature (°C)	Pressure (psi)	Duration (hr)	Starting Material	Products Identified
710	1400	149	Mo,Pe	Cc
754	2000	144	Mo,Pe	Cc
772	1200	114	Fo,Cc	Mo
774	1450	90	Fo,Cc	Mo
774	1800	117	Fo,Cc	Mo
777	2200	67	Mo,Pe	Cc
787	2600	187	Mo,Pe	Cc
787	2500	162	Mo,Pe	Cc
790	2500	95	Fo,Cc	Mo
790	2500	95	Mo,Pe	Cc
790	2100	119	Fo,Cc	Mo
790	2600	144	Mo,Pe	Cc,Fo
790	2300	87	Fo,Cc	Mo
797	2800	163	Mo,Pe	Cc
800	2450	239	Fo,Cc	Mo
800	3100	114	Mo,Pe	Cc
822	2500	118	Fo,Cc	Mo
823	3800	163	Mo,Pe	Cc
829	3000	64	Fo,Cc	Mo
830	3600	89	Mo,Pe	Cc
837	4000	40	Mo,Pe	Cc
838	3700	117	Fo,Cc	Mo
843	4900	69	Mo,Pe	Cc
854	5600	71	Mo,Pe	Cc
857	4800	42	Fo,Cc	Mo
858	5200	114	Mo,Pe	Cc
859	5600	47	Mo,Pe	Cc
880	6800	65	Mo,Pe	Cc,Fo
888	6900	47	Mo,Pe	Cc
898	6900	114	Fo,Cc	Mo
900	7200	96	Fo,Cc	Mo
905	6100	67	Fo,Cc	Mo
910	8700	45	Mo,Pe	Cc
910	9200	48	Mo,Pe	Cc
917	9100	70	Mo,Pe	Cc
920	10,000	46	Mo,Pe	Cc

among the P-T curves is determined by the compositional relations among the phases involved in the reactions according to principles developed by Schreinemakers (Reference 3). One of the six P-T curves which meet at the invariant point represents the reactions of monticellite and forsterite to form periclase and diopside with decreasing temperature. Several runs at temperatures as low as 465°C and 3000 psi  $H_2O$  (water did not enter the reaction) showed that monticellite-forsterite was the stable assemblage since it formed by reaction of periclase and diopside. This indicates that the invariant point, if it occurs, will be below 465°C and that at higher temperatures the curve for the reaction  $Fo + Cc = Mo + Pe + CO_2$  lies at (slightly) higher temperatures than the curve for the reaction  $2Cc + Fo + Di = 3Mo + 2CO_2$ .

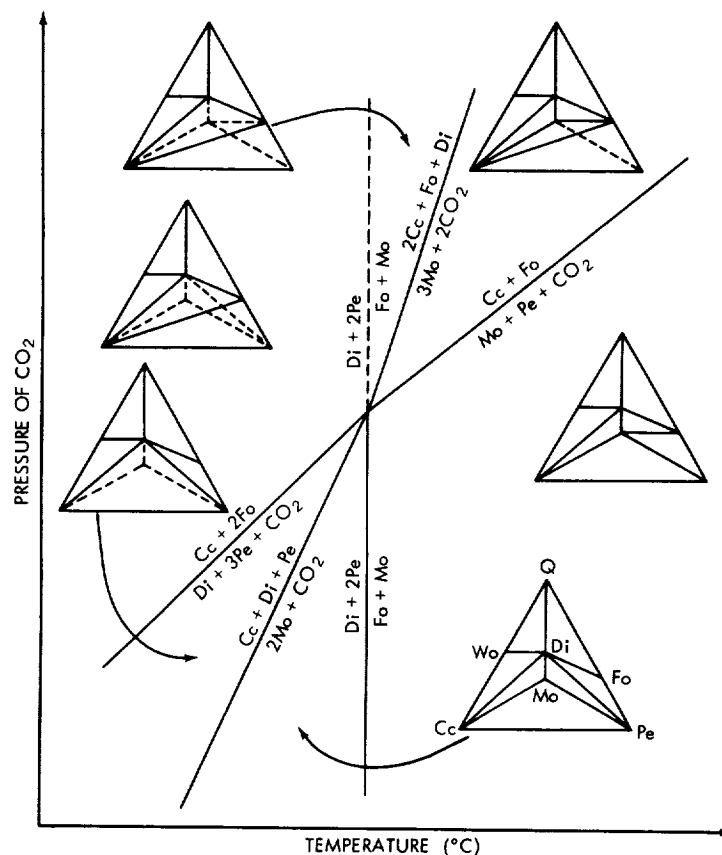


Figure 2—Possible quaternary invariant point involving the phases monticellite, periclase, forsterite, calcite, diopside, and  $CO_2$ .

## DISCUSSION

### Critical Assemblages

Assemblages indicative of temperatures below the curve for the reaction  $Cc + Fo = Mo + Pe + CO_2$  are monticellite-forsterite-calcite- $CO_2$  and forsterite-periclase-calcite- $CO_2$ . These assemblages are replaced, at temperatures above the curve, by forsterite-monticellite-periclase- $CO_2$  and monticellite-periclase-calcite- $CO_2$ .

Forsterite can coexist with calcite, periclase, and  $CO_2$  at temperatures above the curve for the reaction dolomite + calcite = periclase +  $CO_2$  (Reference 4) and at temperatures below the curve for the reaction  $Cc + Fo = Mo + Pe + CO_2$ .

The assemblage monticellite-forsterite-calcite- $CO_2$  is stable only at temperatures above the curve for the reaction  $2Cc + Fo + Di = 3Mo + 2CO_2$ . As previously states, the P-T curve for this reaction lies at temperatures slightly below that of the curve for the reaction  $Cc + Fo = Mo + Pe + CO_2$ . The P-T field of stability of the monticellite-forsterite-calcite- $CO_2$  assemblage is therefore exceedingly small. Solid solution of fayalite in the olivine, however, may cause the limit of this field to be increased by raising the temperature of the reaction, calcite + olivine = Fe-monticellite + periclase +  $CO_2$ .

## Equilibrium Pressure Curves

The above results apply only to the condition in which the pressure on the solid phases is equal to that pressure on a pure fluid phase. If, however, three variables,  $P_f$  (pressure on the fluid phase),  $P_s$  (pressure on the solid phase), and  $T$  (temperature) are considered, the univariant  $P$ - $T$  curve becomes a divariant surface. This surface may be contoured by curves of constant equilibrium pressure ( $P_{E_i}$ ). The equilibrium pressure of component  $i$  of the fluid is defined by Greenwood (Reference 5) as "the pressure of the pure component which is at the same temperature of the system and which has the same chemical potential as the component in the system." This concept was developed by Thompson (Reference 6) and Greenwood (Reference 7) and was applied to components of impure fluid phases by Barnes and Ernst (Reference 8) and Walter (Reference 9). It was applied to decarbonation reactions in the first paper (Reference 2).

Curves of constant equilibrium pressure are presented (Figure 3) for the reaction  $Cc + Fo = Mo + Pe + CO_2$ . Steps in the calculation of values for the slope of these curves are given in Table 2.

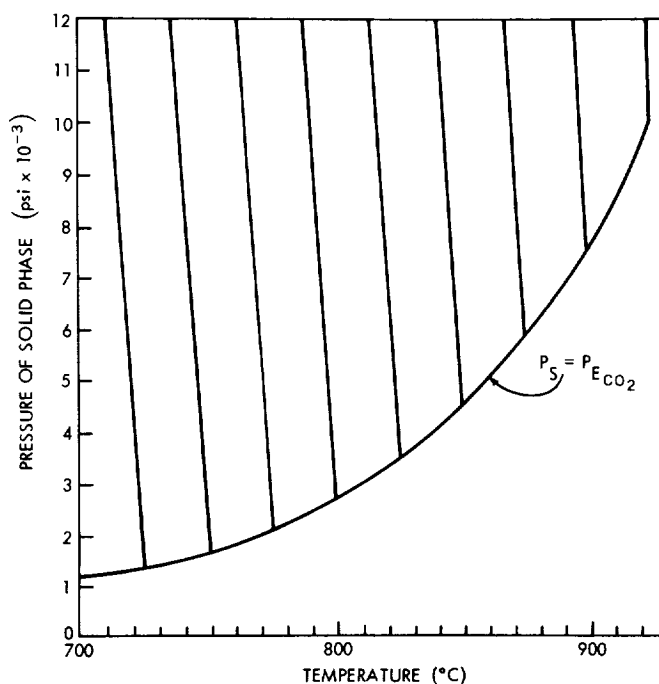


Figure 3—Equilibrium pressure ( $P_{E_{CO_2}}$ ) curves for the reaction  $Cc + Fo = Mo + Pe + CO_2$ .

Table 2  
Steps in the Calculation of  $\left(\frac{\partial P_s}{\partial T}\right)_{P_{E_{CO_2}}}$ .

Temperature (°C)	Pressure (psi)	$\frac{\partial P}{\partial T}$ $\left(\frac{\text{psi}}{^\circ\text{C}}\right)$	$\Delta V^{*}_{CO_2}$ $\left(\frac{\text{cm}^3}{\text{mole}}\right)$	$\Delta V^{*}_{\text{total}}$ $\left(\frac{\text{cm}^3}{\text{reaction}}\right)$	$\Delta S_{\text{total}}$ $\left(\frac{\text{psi-cm}^3}{^\circ\text{C}}\right)$	$\left(\frac{\partial P_s}{\partial T}\right)_{P_{E_{CO_2}}}$ $\left(\frac{\text{psi}}{^\circ\text{C}}\right)$
725	1300	10	960	942	9420	-516
750	1600	14	796	778	10892	-597
775	2200	18.5	598	580	10730	-588
800	2600	30	524	506	15180	-832
825	3400	37	414	396	14652	-803
850	4400	49	332	314	15386	-842
875	5800	58	263	245	14210	-779
900	7400	78	217	199	15522	-851
925	10000	147	170	152	22344	-1225

\*Reference 10.

†Values for the specific volumes of the condensed phases used in this step were as follows: forsterite, 43.73; calcite, 36.92; monticellite, 51.18; periclase, 11.23 ( $\text{cm}^3\text{-gm-mole}$ ).

Table 3

Natural Occurrence of Assemblages Pertinent to the Determined Curve.

Area	Reported Assemblage	Igneous rock Causing metamorphism	Source
Organ Batholith, New Mexico	Fo-Pe-Cc	Quartz monzonite	Dunham, Reference 11
Franklin Mountains, Texas	Cc-Fo-Di	Granite	Lonsdale, Reference 12
Skye, Scotland	Fo-Cc	Granite	Tilley, Reference 13
Vesuvius, Italy	Mo-Cc-Fo	Extrusive	Tilley, Reference 14
Carlingford, Ireland	Cc-Fo-Mo Fo-Pe-Cc	(Not given)	Osborne, Reference 15
Camus Mor, Scotland	Mo-Pe	Olivine gabbro	Tilley, Reference 16

### Natural Occurrence of Pertinent Curves

Naturally occurring assemblages involving the reaction  $Cc + Fo = Mo + Pe + CO_2$ , as well as the type of igneous rock associated with the metamorphism, are given in Table 3. Note that the intrusion of silicic magma generally fails to cause reaction to the high temperature assemblage. On the other hand, metamorphism by an olivine gabbro, in one instance, resulted in the formation of the monticellite-periclase assemblage.

In the reference to the Carlingford district, Osborne (Reference 15) states that the igneous rock type which caused metamorphism is obscure. The assemblages he described occur at a locality in which either a basic igneous series or an acidic magma type could have been responsible for metamorphism. In view of its limited P-T stability field, the occurrence of the calcite-monticellite-forsterite assemblage may help to clarify the petrologic relationships in this district.

### ACKNOWLEDGMENTS

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